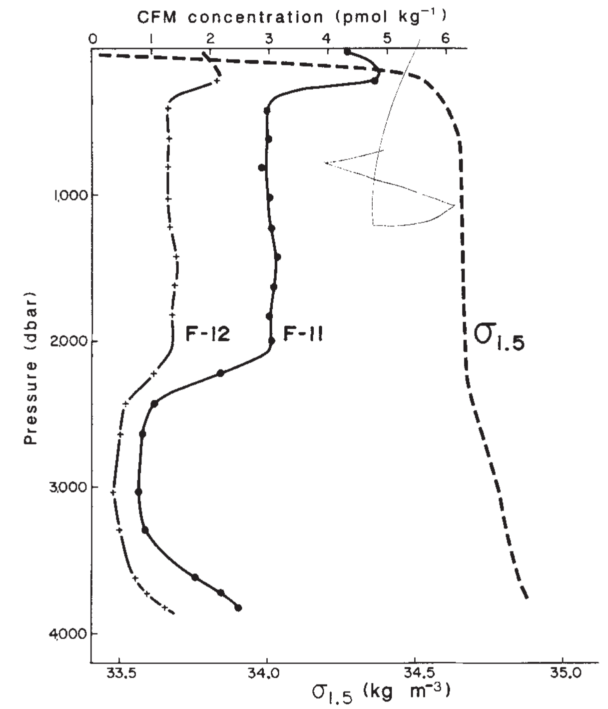

Fig. 4 Vertical profiles of two chlorofluoromethanes CCl_2F_2 (F-12) and CCl_3F (F-11) and $\sigma_{1.5}$ at station 2. A convectively formed deep mixed layer has been covered by an ~500-m-deep layer of water, more typical of the near-surface, southern Labrador Sea. CFMs were measured using purge-and-trap gas chromatography with electron-capture detection[13]. Analytical precision for these data was the greater of: 1% or 0.016 pmol kg^{-1} for F-12, and 1.5% or 0.042 pmol kg^{-1} for F-11, CFM concentrations are reported relative to the SIO (Scripps Institution of Oceanography) 1986 calibration scale (R. F. Weiss, personal communication).

been lower than the initial conditions used with the models. An air-sea CFM flux comparable with the modelled flux could therefore have occurred during the 1985-86 winter, but sufficient to result in only 60% saturation because of the lower initial concentrations. Simulations with the model suggest that the pre-convection inventory of CFM in the upper 2,000 m of the water column at Station 2 might have been only 60-70% of the amount observed there in July-August 1986. In any case, the model results confirm that LSW in its source region does not necessarily attain 100% saturation with respect to CFMs during one year or even two successive years of deep convective renewal.

The concentrations of CFMs in LSW varies both between and within stations. Defining LSW as before, F-11 concentrations ranged from 2.1 to 3.7 pmol kg^{-1}. The mean depth-averaged concentrations in LSW were: 3.05 pmol kg^{-1} (F-11) and 1.32 pmol kg^{-1} (F-12). These values are almost identical to those observed in the deep mixed layer at Station 2 (Fig. 4), and should therefore provide an accurate representation of the initial conditions in LSW during 1986. Use of CFM data as a constraint for ocean circulation models[4] however, will require time series of the CFM content of source waters. Because newly formed LSW has been observed with significantly undersaturated CFM levels, and because the formation process is highly variable in time[1,5] and difficult to model, it seems clear that a CFM source function for LSW cannot be estimated accurately at present. In addition, the historically extreme LSW temperature and salinity characteristics reported here emphasize that even these characteristics are highly variable in time. It is therefore essential that long-term monitoring of CFMs and other tracers be initiated in this region in order that the information contained in their distributions can be exploited.

This research was funded by the Government of Canada, Department of Fisheries and Oceans.

Received 24 August 1987; accepted 4 January 1988.

1. Clarke, R. A. & Gascard, J.-C. *J. phys. Oceanogr.* **13**, 1764-1778.
2. Talley, L. D. & McCartney, M. S. *J. phys. Oceanogr.* **12**, 1189-1205 (1982).
3. Weiss, R. F., Bullister, J. L., Gammon, R. H. & Warner, M. J. *Nature* **314**, 608-610 (1985).
4. Woods, J. D. *Nature* **314**, 501-511 (1985).
5. Lazier, J. R. N. *Atmos.-Ocean* **18**, 227-238 (1981).
6. Clarke, R. A. & Coote, A. R. *J. phys. Oceanogr.* (in the press).
7. Gascard, J.-C. & Clarke, R. A. *J. phys. Oceanogr.* **13**, 1779-1797 (1983).
8. Gordon, A. L. *J. phys. Oceanogr.* **8**, 600-612 (1978).
9. Roether, W. in *Dynamic Processes in the Chemistry of the Upper Ocean* (eds Burton, J. D., Brewer, P. G. & Chesselet, R.) 117-128 (Plenum, New York, 1986).
10. Warner, M. J. & Weiss, R. F. *Deep Sea Res.* **32**, 1485-1497 (1985).
11. Smith, S. D. & Dobson, F. W. *Atmos.-Ocean* **22**, 1-22 (1984).
12. Shuhy, J. L. *Oceanographic Report No. CG373-78, Oceanographic Observations North Atlantic Ocean Station Bravo, Terminal Report 1964-1974* (US Coast Guard Oceanography Unit, Washington DC, 1978).
13. Wallace, D. W. R. & Moore, R. M. *J. geophys. Res.* **90**, 1155-1166 (1985).

Mass extinctions, atmospheric sulphur and climatic warming at the K/T boundary

Michael R. Rampino*† & Tyler Volk*

* Department of Applied Science, New York University, New York, New York 10003, USA
† NASA, Goddard Space Flight Center, Institute for Space Studies, New York, New York 10025, USA

A connection has recently been proposed between cloud albedo over the oceans and the release of dimethyl sulphide (DMS) by marine algae. DMS acts as a precursor for most of the cloud condensation nuclei (CCN) in the marine atmosphere[1]. The mass extinctions at the Cretaceous/Tertiary (K/T) boundary include about 90% of marine calcareous nannoplankton[2,3], and carbon isotope data show that marine primary productivity as a whole was drastically reduced for at least several tens of thousands of years, and perhaps up to a million years after the extinction event[4–6]. The elimination of most marine calcareous phytoplankton would have meant a severe decrease in DMS production, leading to a drastic reduction in CCN and hence marine cloud albedo. Here we examine the possible climatic effects of a drastic decrease in CCN associated with a severe reduction in the global marine phytoplankton abundance. Calculations suggest that a reduction in CCN of more than 80%, and the resulting decrease in marine cloud albedo, could have produced a rapid global warming of 6 °C or more. Oxygen isotope analyses of marine sediments from many parts of the world have been interpreted as indicating a marked warming coincident with the demise of calcareous nannoplankton at the K/T boundary. Decreased marine cloud albedo, and resulting high sea surface temperatures could have been a factor in the maintenance of low productivity in the 'Strangelove Ocean' period following the K/T extinctions.

Charlson *et al.*[1], and subsequent work[7], have shown that the precursor for most CCN over the oceans is the DMS released by marine phytoplankton, which oxidizes to form a sulphate aerosol. If the total liquid water content in the clouds is held constant, changes in the number density of CCN would affect the cloud droplet size, which affects the cloud albedo. Their model[1] has quantified the effects of either increasing the number density of cloud droplets, which increases the cloud albedo, or decreasing the number density with its associated decrease in the cloud albedo.

We use the model results from Charlson *et al.* (their Fig. 1), which show the effect upon stratiform top-of-cloud albedo due to variations in the CCN number density. Following their example, these albedo variations have been converted to changes in solar albedo at the top of the atmosphere averaged over the

Earth's surface, and then into equivalent variations in the solar constant. The range spanned by these equivalent solar constant variations ($1.0 \leq S/S_0 \leq 1.06$) corresponds to the range studied by Wetherald and Manabe[8] with a general circulation model (GCM). We therefore apply their results to convert the equivalent solar constant variations into associated variations in global average surface temperature (ΔT). Figure 1 shows these variations as a function of normalized DMS concentration for $0.1 \leq [DMS]/[DMS]_{ref} \leq 1.0$. (It was not possible to extrapolate the results of Charlson *et al.* to values < 0.1, but these would give somewhat higher temperatures.) Figure 1 shows the results for reference top-of-cloud albedos of 0.3, 0.5 and 0.7, which span the range of satellite-derived albedos over marine stratus and stratocumulus[1].

The GCM results of Wetherald and Manabe[8] give a climate sensitivity (the slope of the $\Delta T(S/S_0)$ curve) of 2.2 °C per 1% change in the solar constant when $S = S_0$, which is higher than the value of 1.85 (from an earlier paper by Wetherald and Manabe[9]) applied by Charlson *et al.*, but consistent with the value of 2.0 found by another GCM study of Hansen *et al.*[10]. Also, the climate sensitivity of Wetherald and Manabe is not constant, but smoothly decreases to 0.9 when $S = 1.06S_0$. Climate sensitivity was found to behave differently in a GCM study of the Cretaceous[11], in which the climate sensitivity to a quadrupling of CO_2 was actually higher by 33% in the Cretaceous than in the present-day model. This increase in sensitivity is probably the result of the greater importance of water vapour climate feedback in the Cretaceous experiment, due to higher reference temperatures and the nonlinear relationship between surface temperature and saturation vapour pressure. Here we use the Wetherald and Manabe[8] results as a reasonable method for converting solar constant variations to global temperatures, and note that even if the temperatures associated with the smallest values of $[DMS]/[DMS]_{ref}$ in Fig. 1 were decreased by several °C due to possible negative feedbacks[1,7], our conclusions would remain essentially the same.

Figure 1 shows that for DMS concentrations < 20% of the reference value, global temperatures could rise by $\gtrsim 6$ °C, and, depending upon top-of-cloud albedo, by nearly 10 °C when DMS is reduced to 10% of the reference value. Even a 50% reduction in DMS would produce a significant global warming of ~3-4 °C. The thermal mass and mixing structure of the ocean would delay the full surface warming by only several thousand years. These results indicate that a drastic reduction in DMS production, if maintained, could lead to a substantially warmer Earth essentially simultaneous with a phytoplankton extinction event.

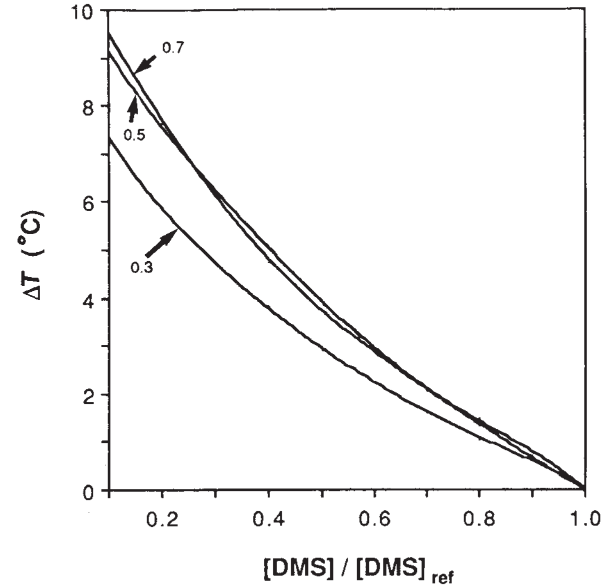

Fig. 1 Change of globally averaged surface temperature as a function of normalized DMS concentration, assumed equivalent to global DMS production rate by phytoplankton. These results were obtained from the model of Charlson *et al.*[1] relating the visible albedo at the top of the reference cloud to the number density of cloud droplets (assumed equivalent to DMS concentration) (see Fig. 1 in ref. 1). Their model used a reference cloud droplet radius of 8 μm, but they stated that the results are still valid within 20% for droplet radii within the range found in real clouds (4-500 μm). Then, following the technique shown in their Table 1, the changes in top-of-cloud albedo for oceanic stratiform water clouds were converted to equivalent changes in the solar constant by multiplying sequentially by factors of 0.81 (to convert top-of-cloud albedo to solar albedo at the top of the atmosphere), 0.31 (to convert from the area covered by oceanic stratiform water clouds to an average over the Earth's surface area) and 1/(1 − present planetary albedo) = 1.43 (to convert from the planetary albedo change to equivalent change in the solar constant, where the present planetary albedo is taken as 0.3). Finally, we used the GCM model results of Wetherald and Manabe[8] (see their Table 8 and Fig. 20 for the model with variable clouds) to calculate the global average surface temperatures for the various values of the equivalent solar constant. Curves are shown for three different values (0.3, 0.5 and 0.7) of the visible albedo at the top of the reference cloud.

Two separate pieces of evidence point to a trauma in the global marine biosphere 66 million years ago, at the K/T boundary. First, a number of studies report a negative anomaly in $\delta^{13}C$ of up to 3‰ in the carbonate fine fraction (< 63 μm, largely nannoplankton debris), and in individual planktonic foraminifera, in K/T boundary sediments. This anomaly appears to be a worldwide phenomenon[12-18], and suggests a surface ocean of very low primary productivity, the so-called 'Strangelove Ocean'[16,18]. In the South Atlantic Deep Sea Drilling Project (DSDP) Site 524, the carbon isotope anomaly begins just above the K/T boundary (as marked by an iridium anomaly in a thin boundary clay) and reaches the minimum value ~40,000-50,000 years later[4]; $\delta^{13}C$ values did not return to their pre-boundary values for at least 300,000-400,000 years. The magnitude of the $\delta^{13}C$ decrease varies from locality to locality, and it has been detected solely in surface-water calcareous organisms. Arthur *et al.*[6] suggest that the significant reduction in surface-ocean primary productivity lasted more than 1 Myr after the K/T boundary.

Second, the K/T boundary is marked by a drastic reduction in $CaCO_3$ deposition in the deep sea[6] reflecting mainly the mass extinction of calcareous nannoplankton and foraminifera. Calcium carbonate deposition was reduced for at least 350,000 years[4], and in some cases for as long as 1 Myr[6]. According to Zachos and Arthur[18], this decrease in carbonate was the result of a severe decrease in surface primary production, not a long-term dissolution event.

The DMS production per unit productivity seems to vary significantly among species[19] (M. O. Andreae, personal communication). Thus, the general correspondence between DMS and primary productivity (for example, relatively high DMS in upwelling regions[19]) might be due to a roughly constant ecological mix of high- and low-DMS producers. DMS flux to the atmosphere has been shown to be correlated seasonally and regionally with solar flux[7], but solar flux also drives productivity, especially seasonally in high latitudes. The inference of a decrease in DMS associated with a global collapse of primary productivity as shown by the $\delta^{13}C$ data across the K/T boundary requires only the reasonable assumption of some regularity in the mix of high- and low-DMS producers on both sides of the boundary. However, because Andreae (personal communication) has proposed that the calcareous nannoplankton are one of the main or perhaps even the dominant producers of DMS, the mass extinction of this group at the boundary is strong evidence for a significant change in DMS flux.

Is the predicted surface warming observed? Oxygen isotope analyses across the K/T boundary give differing results. A number of analyses suggest a possible negative excursion of $\leq 2.5‰$ in $\delta^{18}O$ at or just above the K/T boundary, which in some cases is coincident with the most negative $\delta^{13}C$ anomaly in the boundary sections[4,15,17,20-22]. Assuming that a 0.2‰ decrease in $\delta^{18}O$ represents a 1 °C temperature increase, this negative $\delta^{18}O$ excursion has been interpreted as possibly indicating a dramatic warming of ocean surface waters by as much as 10-12 °C (refs 4, 5, 15, 20, 21).

For example, boundary sections in Spain at Caravaca, Sopelana and Zumaya show maximum negative $\delta^{18}O$ excursions in bulk carbonate samples, at or just above the K/T boundary, ranging from -1.4 to $-2.4‰$, corresponding to warmings of ~7-12 °C, closely correlated with the maximum negative $\delta^{13}C$ excursion[15,21,23]. Similarly, bulk carbonate in the section at Biarritz, France shows a maximum negative $\delta^{18}O$ excursion of ~1.5‰ across the boundary, whereas the boundary sequence at Lattengebirge in southwestern Germany, although possibly affected by diagenesis, has a possible maximum negative $\delta^{18}O$ departure of $-2.5‰$, in both cases corresponding to the maximum negative excursion in $\delta^{13}C$[15]. In the South Atlantic, at DSDP Site 524, Hsü *et al.*[4] report an average $\delta^{18}O$ excursion in the carbonate fine fraction of $-0.4‰$ between pre- and post-boundary samples, with a difference of $-2‰$ between extremes in the standard deviation, suggesting warmings of at least 2 °C and possibly up to 10 °C. The maximum negative excursion in $\delta^{18}O$ occurs at about the same level as the most negative $\delta^{13}C$ anomaly, in the Lower Palaeocene[4]. A negative departure of ~1‰ in $\delta^{18}O$ in benthic foraminifera, in some sections, at about the same time indicates possible warming of ocean bottom waters of ≤ 5 °C over late Cretaceous values[5,20]. In general, the inferred sea surface temperature increases seem to be greater in European and Atlantic sites than in the Pacific[15,18].

In contrast, other studies of K/T boundary sections have not identified a marked negative $\delta^{18}O$ departure[18,23,24], and the $\delta^{18}O$ anomaly in some sections has been interpreted as a selective diagenetic overprint[18,22]. One would expect, however, that the magnitude of the temperature increase, and hence the oxygen isotope anomaly, might vary considerably from site to site, as seen in the record. The increase in surface water temperatures might be suppressed in the tropics, if most of the increased solar energy received there goes into evaporation, and not into sensible heating[25]. It may be significant, therefore, that the evidence for little or no increase in sea surface temperatures comes from the sections at the lowest palaeolatitudes, DSDP sites 47.2 and 577 at ~20° N palaeolatitude, and DSDP site 465 at ~15° N palaeolatitude, in the Pacific. It should also be recognized that the early Danian seems to have been a time of unstable and fluctuating oceanographic and climatic conditions[4,15,18], and some sections perhaps contain hiatuses. For example, several of the DSDP sites studied by Zachos and Arthur[18] have no measurable iridium anomaly, suggesting the possible incompleteness of these boundary sections.

The occurrence of a significant negative $\delta^{18}O$ anomaly in boundary sections from various parts of the world, and the coincidence of the oxygen isotope anomaly with the marked negative $\delta^{13}C$ anomaly in a number of boundary sections[4,15,21,22] suggest that the oxygen isotope anomaly is not a local diagenetic feature. Diagenesis cannot be ruled out as a factor in the apparent $\delta^{18}O$ fluctuations in some sections, and further isotope analyses on sequences with high sedimentation rates, shallow burial and no apparent hiatuses at the K/T boundary are needed to resolve the problem[18]. Deep Sea Drilling sites in relatively high palaeolatitudes might be the best sections for oxygen isotope analyses designed to test further for a significant warming in sea surface temperatures at the K/T boundary (J. Zachos, personal communication).

Several authors have suggested that a greenhouse warming from increased atmospheric CO_2 and/or H_2O could have taken place at the K/T boundary[26-28], and Kasting *et al.*[29] have modelled the possible global temperature increase from elevated atmospheric CO_2 following an impact event. We believe that the considerable decrease in marine cloud albedo predicted here could have provided an independent mechanism for climate warming, which could significantly enhance any possible warming resulting from increases in atmospheric greenhouse gases. The model proposed here could be further tested with global climate model sensitivity studies of the effects of changes in marine cloud albedo on sea temperatures using reconstructed late Cretaceous boundary conditions[11,30]. The available evidence suggests that the extinction of virtually all late Cretaceous calcareous nannoplankton and, as inferred from the $\delta^{13}C$ record, the drop in global productivity by phytoplankton, in general, could have precipitated a severe warming. This heating, and its destabilizing effects on global climate, combined with the proposed impact-induced[31], and possibly related volcanic[32,33] trauma at the boundary could have inhibited the full recovery of the marine biosphere, and may have contributed to the initiation and maintenance of Strangelove Ocean conditions for the observed period of $\geq 10^5$ years.

Similar carbon isotope anomalies have been reported at other major geological boundaries; the Precambrian/Cambrian[34-37], the Devonian/Carboniferous[38] and the Permian/Triassic[39] (although their significance has been questioned[40,41]). It may be, therefore, that episodes of reduced marine cloud albedo and related global warmings accompanied other mass extinctions in the geological record, and these may be detectable through careful palaeotemperature analyses at these boundaries.

We thank K. Caldeira, M. I. Hoffert, R. B. Stothers, S. Warren and J. C. Zachos for helpful discussions, and M. O. Andreae for a review. Research support for M.R.R. was provided by the Center for Global Habitability at Columbia University. T.V. was supported by NASA.

Received 21 September 1987; accepted 7 January 1988.

1. Charlson, R. J., Lovelock, J. E., Andreae, M. O. & Warren, S. G. *Nature* **326**, 655-661 (1987).
2. Thierstein, H. R. *Spec. Publ. Soc. Econ. Miner. Petrol.* **32**, 355-394 (1981).
3. Thierstein, H. R. *Spec. Pap. geol Soc. Am.* **190**, 385-399 (1982).
4. Hsü, K. J. *et al. Science* **216**, 249-256 (1982).
5. Hsü, K. J., McKenzie, J. A. & He, Q. X. *Spec. Pap. geol Soc. Am.* **190**, 317-328 (1982).
6. Arthur, M. A., Zachos, J. C. & Jones, D. S. *Cret. Res.* **8**, 43-54 (1987).
7. Bates, T. S., Charlson, R. J. & Gammon, R. H. *Nature* **329**, 319-321 (1987).
8. Wetherald, R. T. & Manabe, S. *J. atmos. Sci.* **37**, 1485-1510 (1980).
9. Wetherald, R. T. & Manabe S. *J. atmos. Sci.* **32**, 2044-2059 (1975).
10. Hansen, J., E. *et al.* in *Climate Processes and Climate Sensitivity* (eds Hansen, J. E. & Takahashi, T.) 130-163 (Am. Geophys. Union, Washington, DC, 1984).
11. Barron, E. J. & Washington, W. M. in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present* (eds Sundquist, E. T. & Broecker, W. S.) 546-553 (Am. Geophys. Union, Washington, DC, 1985).
12. Brennecke, J. L. & Anderson, T. F. *Am. geophys. Union Trans.* **58**, 415 (1977).
13. Thierstein, H. R. & Berger, W. H. *Nature* **276**, 461-466 (1978).
14. Scholle, P. A. & Arthur, M. A. *Am. Ass. Petrol. Geol. Bull.* **64**, 67-87 (1980).
15. Perch-Nielsen, K., McKenzie, J. & He, Q. X. *Spec. Pap. geol. Soc. Am.* **190**, 353-371 (1982).
16. Hsü, K. J. & McKenzie, J. A. in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present* (eds Sundquist, E. T. & Broecker, W. S.) 487-492 (Am. Geophys. Union, Washington, DC, 1985).
17. Hsü, K. J. in *Mesozoic and Cenozoic Oceans* (ed. Hsu, K. J.) 75-84 (Am. Geophys. Union, Washington, DC, 1986).
18. Zachos, J. C. & Arthur, M. A. *Paleoceanogr.* **1**, 5-26 (1986).
19. Andreae, M. O. in *The Role of Air-Sea Exchange in Geochemical Cycling* (ed. Buat-Ménard, P.) 331-362 (Reidel, Dordrecht, 1986).
20. Boersma, A. *et al. Init. Rep. DSDP* **43**, 695-718 (1979).
21. Smit, J. *Spec. Pap. geol. Soc. Am.* **190**, 329-352 (1982).
22. Margolis, S. V. *et al. Paleoceanogr.* **2**, 361-377 (1987).
23. Boersma, A. & Shackleton, N. J. *Init. Rep. DSDP* **62**, 513-526 (1981).
24. Zachos, J. C. *et al. Init. Rep. DSDP* **86**, 513-532 (1985).
25. Hoffert, M. I. *et al. J. atmos. Sci.* **40**, 1659-1668 (1983).
26. McLean, D. M. *Science* **201**, 401-406 (1978).
27. McLean, D. M. *Cret. Res.* **6**, 235-259 (1985).
28. Emiliani, C., Kraus, E. B. & Shoemaker, E. M. *Earth planet. Sci. Lett.* **55**, 317-334 (1981).
29. Kasting, J. F., Richardson, S. M., Pollack, J. B. & Toon, O. B. *Am. J. Sci.* **286**, 361-389 (1986).
30. Glancy, T. J. Jr, Barron, E. J. & Arthur, M. A. *Paleoceanogr.* **1**, 523-537 (1986).
31. Alvarez, W. *Eos* **67**, 649-658 (1986).
32. Courtillot, V. *et al. Earth planet Sci. Lett.* **80**, 361-374 (1986).
33. Rampino, M. R. *Nature* **327**, 468 (1987).
34. Hsü, K. J. *et al. Nature* **316**, 809-811 (1985).
35. Margaritz, M. *et al. Nature* **320**, 258-259 (1986).
36. Tucker, M. E. *Nature* **319**, 48-50 (1986).
37. Aharon, P., Schidlowski, M. & Singh, I. B. *Nature* **327**, 699-702 (1987).
38. Sun Yijin *et al.* in *Contr. 27th Int. Geol. Congr.* 225-234 (Science Press, Beijing, 1984).
39. Dao-Yi, X. *et al. Nature* **321**, 854-855 (1986).
40. Awramik, S. M. *Nature* **319**, 696 (1986).
41. Morris, S. C. & Bengtson, S. *Nature* **319**, 696-697 (1986).